

(19) World Intellectual Property Organization  
International Bureau



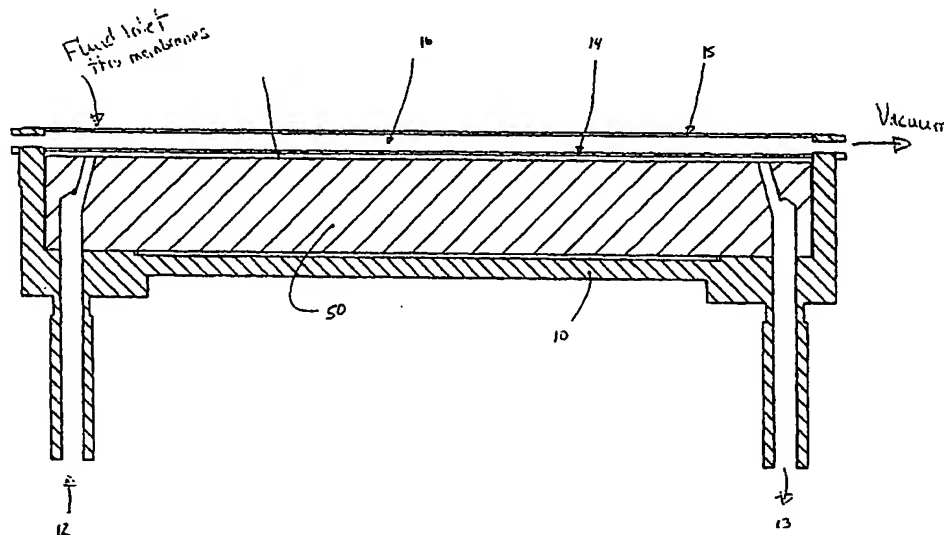
(43) International Publication Date  
14 December 2000 (14.12.2000)

PCT

(10) International Publication Number  
**WO 00/75402 A1**

- (51) International Patent Classification<sup>7</sup>: C25B 9/00, 11/03, 11/04, 13/00, C25D 5/00, 5/20
- (21) International Application Number: PCT/US00/14976
- (22) International Filing Date: 31 May 2000 (31.05.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
60/137,558 4 June 1999 (04.06.1999) US
- (71) Applicant (for all designated States except US): MILLIPORE CORPORATION [US/US]; 80 Ashby Road, Bedford, MA 01730 (US).
- (72) Inventor; and
- (75) Inventor/Applicant (for US only): STOCKBOWER, David, Windsor [US/US]; 297 Commercial Street, Braintree, MA 02184 (US).
- (74) Agents: LEMACK, Kevin, S. et al.; Nields, Lemack & Dingman, Suite 8, 176 E. Main Street, Westboro, MA 01581 (US).
- (81) Designated States (national): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:  
— With international search report.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: HYDROPHOBIC AND HYDROPHILIC MEMBRANES TO VENT TRAPPED GASES IN A PLATING CELL



(57) Abstract: A plating tool cell anode for venting unwanted gases from a fluid plating solution. In a first embodiment, the solution is introduced into a chamber, defined by the plating tool cell (10), by fluid inlet (12) and contacts the anode (50). The fluid encounters a hydrophobic membrane (14) and a hydrophilic membrane (15) spaced from the hydrophobic membrane. A driving force, such as a vacuum, is applied to the gap (16) between the membranes to remove unwanted gases therein. In a second embodiment, a single membrane is used that is both hydrophobic and hydrophilic. Preferably, the hydrophobic portion of the membrane is located at or near the perimeter of the chamber and gas to be vented is directed toward the hydrophobic portion(s).

Best Available Copy

WO 00/75402 A1

HYDROPHOBIC AND HYDROPHILIC MEMBRANES TO VENT  
TRAPPED GASES IN A PLATING CELL

BACKGROUND OF THE INVENTION

5 In semiconductor manufacturing, a plating tool uses a negatively charged anode (usually a copper anode) to plate a positively charged (cathode) silicon wafer. The anode provides a source of replenishing metal ions. At the cathode, the metal ions are reduced to metal and deposited on the cathode surface. Sulfuric acid and a plating solution flows through a chamber around the anode and is used to dissolve a metal (copper) plate. As fluid flows past the anode, it becomes enriched with metal ions.

10 During the chemical reaction that dissolves the metal (e.g., copper), hydrogen gas is liberated. In addition, entrapped gases are generally present during start-up. These gases must be vented so that they do not effect the electrical field or the wafer plating uniformity. Indeed, a separate upstream degasser removes most dissolved air from the main fluid flow path. The generated hydrogen gas, if not removed, becomes entrapped in the plating solution as bubbles or microbubbles and may interfere with the plating operation.

15 It therefore would be desirable to provide a means for venting hydrogen gas and any other trapped gases out of the plating solution before the solution reaches the wafer.

SUMMARY OF THE INVENTION

20 The problems of the prior art have been overcome by the present invention, which provides a plating anode cup filter design that vents unwanted gases from the plating solution before they exit the cell and reach the wafer. More specifically, in a first embodiment of the present invention, in the chamber where the fluid flows into the plating tool cell and contacts the anode, it encounters a hydrophobic membrane and a hydrophilic membrane spaced from the hydrophobic membrane. A driving force such as a vacuum applied in the space between the membranes removes unwanted gases therein.

In a second embodiment of the present invention, a single membrane is used that is both hydrophobic and hydrophilic. Preferably the hydrophobic portion of the membrane is located at or near the perimeter of the fluid chamber in the plating tool cell, and gas to be vented is directed toward the hydrophobic portion(s).

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a cross-sectional view of the anode holder in accordance with the present invention;

Figure 2 is a cross-sectional view of the anode holder in accordance with another embodiment of the present invention;

Figure 3 is a top view of a membrane having hydrophilic and a hydrophobic portions in accordance with one embodiment of the present invention;

Figure 4 is a cross-sectional view of an anode holder using the membrane of Figure 3; and

Figure 5 is a cross-sectional view of still another embodiment of the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

Turning now to Figure 1, there is shown an anode for use in semiconductor manufacturing. A plating tool cell 10 is the housing for the anode 50, which is preferably a copper anode, and includes one or more fluid inlets 12. Thus, the plating tool cell 10 serves as an anode holder and as a means for fluid distribution to the substrate being plated, such as a wafer (not shown) which is typically rotating for uniform plating. Preferably the plating tool cell 10 is made of plastic, and includes an optional fluid inlet 12 and a fluid outlet 13.

A fluid plating solution or ion source, such as copper sulfate, is introduced into a chamber defined by the plating tool cell 10 through optional fluid inlet 12, and contacts the anode 50. The resulting reaction between the plating solution and the metal anode generates hydrogen gas. In the embodiment shown, situated in the fluid path is a hydrophobic membrane 14. The hydrophobicity of the membrane 14 inhibits or prevents

passage of the fluid. However, the porosity of the hydrophobic membrane 14 is such that gases, generally air and hydrogen, entrapped in the fluid are able to pass through the hydrophobic membrane 14 easily. A second membrane 15 is positioned downstream of the first membrane (in the direction away from the anode 50). The second membrane 15 is spaced from the first membrane 14, and is hydrophilic. Once the hydrophilic membrane 15 is wetted, it does not allow the passage of gases through it. Accordingly, most or all of the gases remain in the gap 16 between the two membranes. The gap 16 can be filled with a open mesh type separation material, and may be 1/16 to 1/4 inch wide, on average. A driving force such as a vacuum source in communication with the gap 16 with suitable plumbing draws off the gases, thereby preventing them from contacting the wafer and causing defects. Alternatively, high velocity air can be used to create a vacuum by the venturi effect to draw off the gases. Figure 2 shows another embodiment where the gases are vented in gap 16 by creating a high spot 23 in the gap 16 mechanically. The high spot 23 is a portion of the gap 16 that is wider, from membrane 14 to membrane 15, than the total average width of the gap 16. The air tends to collect in the high spot 23 and vent naturally, or can be assisted with a vacuum or high velocity air pressure. The high spot 23 also can be created by bowing the membrane with external fluid pressure, leaving high spots during processing.

Figure 3 illustrates another embodiment of the present invention. In this embodiment, the membrane 14' is patterned such that only a portion 28 thereof is hydrophobic. Conventional techniques to render portions of the membrane hydrophobic well known to those skilled in the art can be used. Preferably, the hydrophobic portion(s) are located at or near the perimeter of the cell 10, and the fluid flow is directed towards the perimeter, as shown in Figure 4.

Figure 5 illustrates another embodiment of the present invention, where a high spot 23 is created and a small hydrophobic membrane patch 15' is used in a vertical orientation. The hydrophobic membrane 15 is optional, and a

bowed hydrophilic membrane 14 is positioned to create a high spot 23 as in the embodiment of Figure 2. The air trapped in gap 16 vents naturally through hydrophobic patch 15' without the use of an external driving force such as a vacuum.

- 5        The removal of bubbles from the plating solution prior to their reaching the wafer contributes to lower plating defects on the wafer.

What is claimed is:

1. An anode plating cell, comprising:

an anode;

5 a housing for said anode, said housing having a fluid inlet and a fluid outlet;

a hydrophobic membrane in said housing downstream of said anode;

a hydrophilic membrane in said housing downstream of and spaced from said hydrophobic membrane by a gap;

10 whereby gases entrapped in said fluid pass through said hydrophobic membrane into said gap and are prevented from passing through said hydrophilic membrane.

2. The anode plating cell of claim 1, further comprising a driving force for removing said entrapped gases from said gap.

15 3. The anode plating cell of claim 2, wherein said driving force is a vacuum.

4. The anode plating cell of claim 1, wherein said anode comprises copper.

20 5. An anode plating cell, comprising:

an anode;

a housing for said anode, said housing having a fluid inlet and a fluid outlet;

25 a membrane in said housing downstream of said anode, said membrane having a hydrophobic portion permeable to said fluid and to gases entrapped in said fluid, and a hydrophilic portion permeable to said fluid but not to said gases.

6. The anode plating cell of claim 5, further comprising a driving force for removing said entrapped gases from said housing.

30 7. The anode plating cell of claim 6, wherein said driving force is a vacuum.

8. The anode plating cell of claim 5, wherein said anode comprises copper.

35 9. A method of removing gases entrapped in a plating solution from an anode plating cell, comprising:

providing an anode in said cell;

providing a hydrophobic membrane in said cell downstream of said anode;

providing a hydrophilic membrane in said cell spaced from and downstream of said hydrophobic membrane;

5 circulating plating solution in said anode plating cell to contact said plating solution with said anode;

causing gases entrapped in said plating solution to pass through said hydrophobic membrane but not through said hydrophilic membrane; and

10 removing said gases from said cell.

10. A method of removing gases entrapped in a plating solution from an anode plating cell, comprising:

providing an anode in said cell;

circulating a plating solution in said cell;

15 causing said plating solution to contact said anode;

providing a membrane in said cell downstream of said anode, said membrane having a hydrophobic portion permeable to said plating solution and to entrapped gases in said plating solution, and a hydrophilic portion permeable to said plating solution but not to gases entrapped in said plating solution;

20 causing gases entrapped in said plating solution to pass through said hydrophobic portion of said membrane but not through said hydrophilic portion; and

removing said gases from said cell.

25

1/4

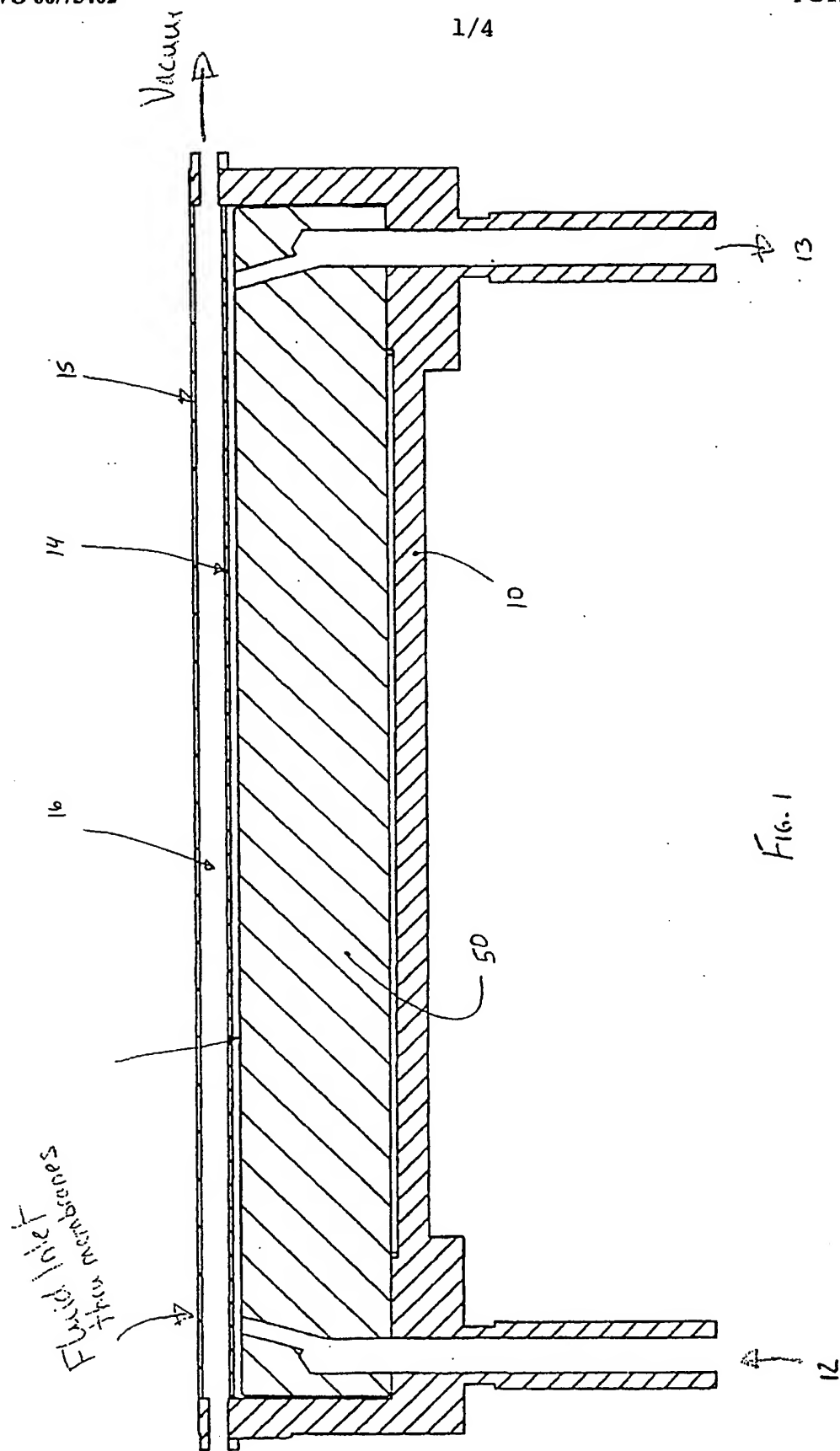
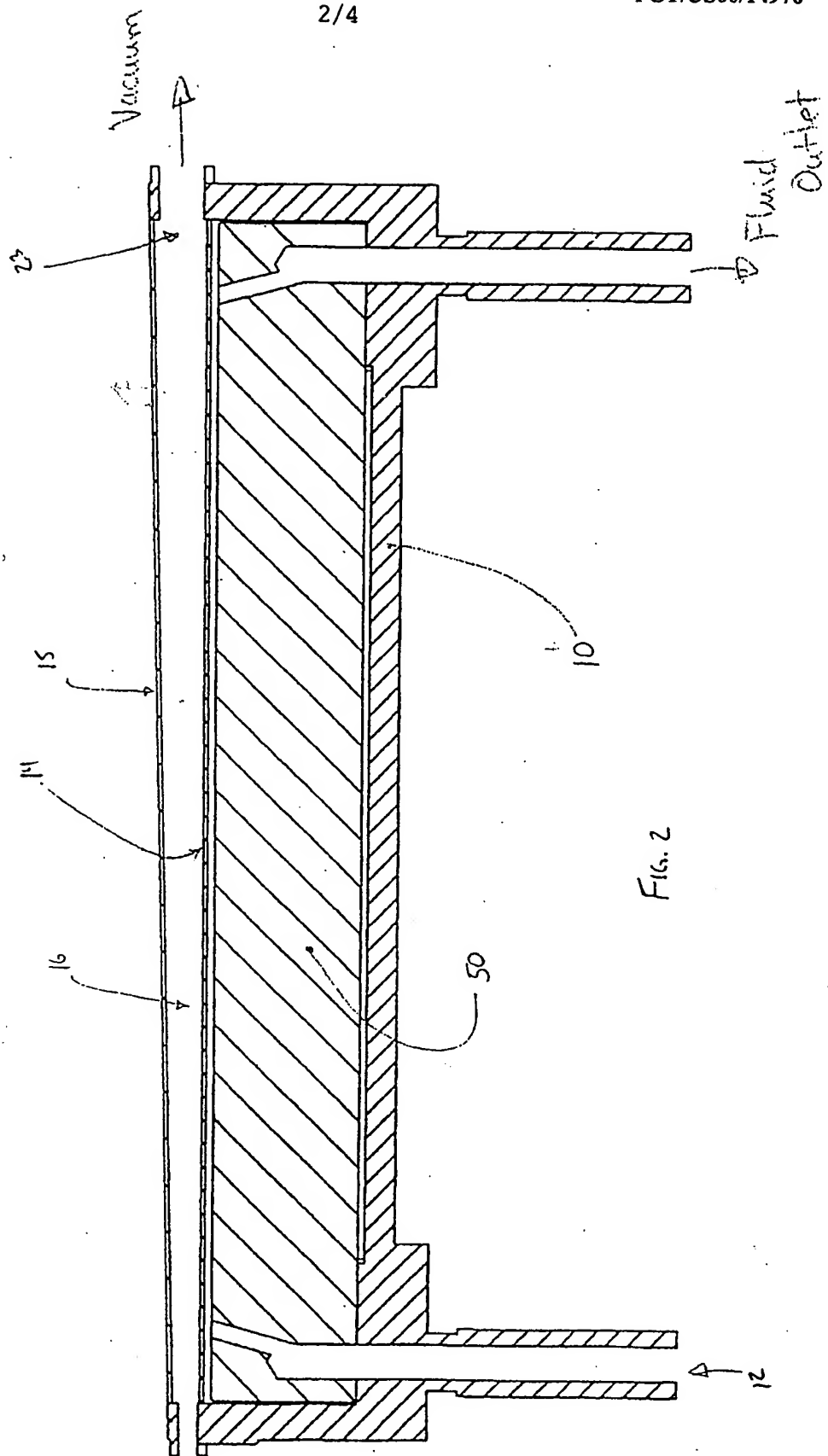


Fig. 1

Fluid inlet  
membranes





3/4

Fig. 3

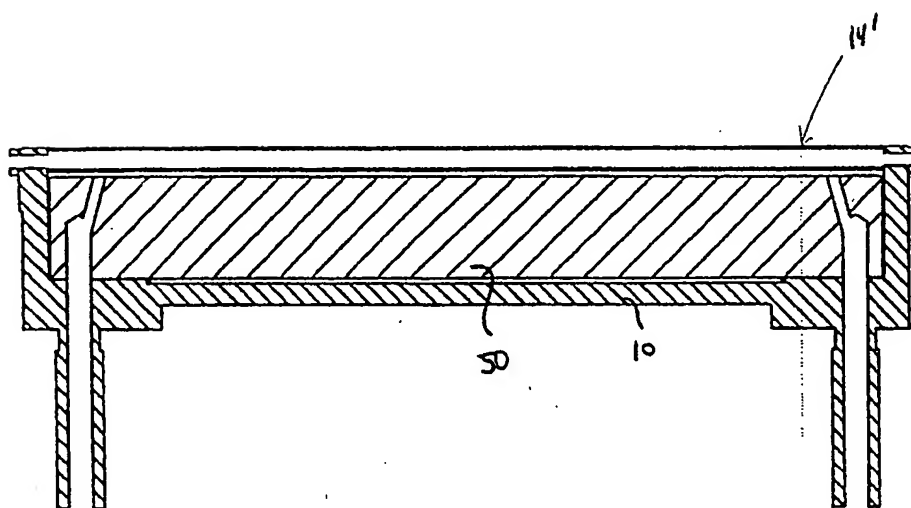
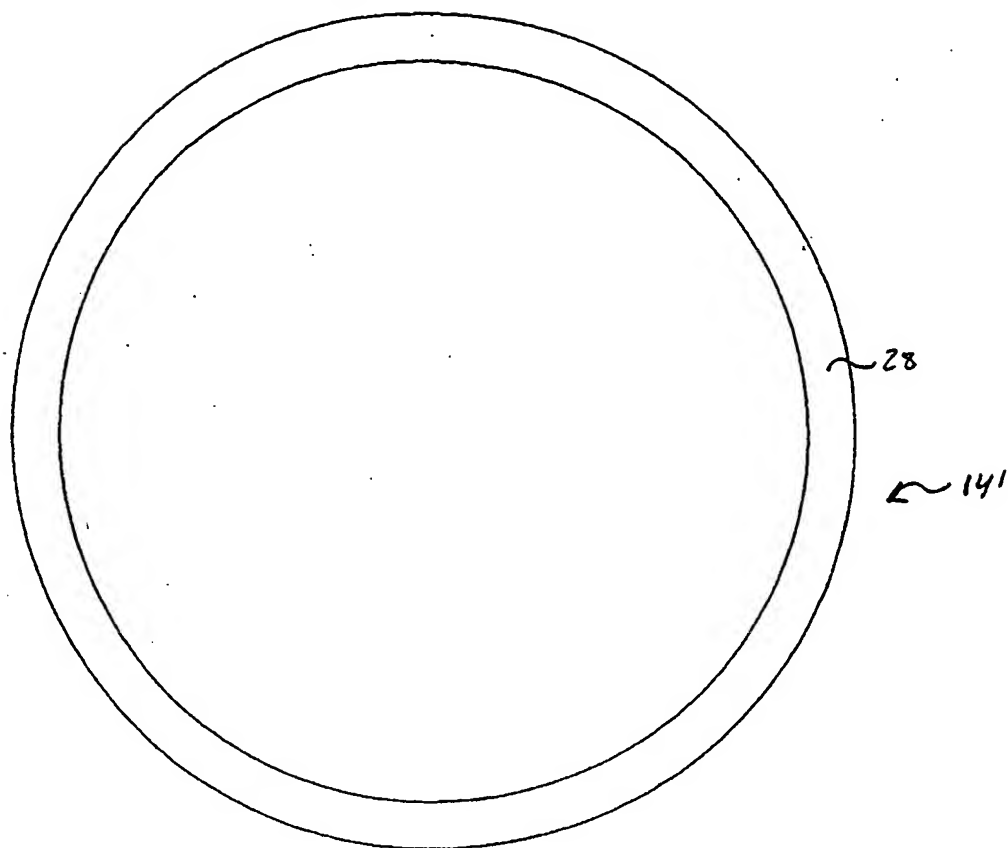


Fig. 4



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/14976

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) : C25B 9/00, 11/03, 1104, 13/00; C25D 5/00, 5/20

US CL : 204/266, 270, 278, 282, 283, 292; 205/88, 148, 338, 350

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 204/266, 270, 278, 282, 283, 292; 205/88, 148, 338, 350

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,201,653 A (O'NEILL et al) 06 May 1980, see Figures and col. 4, lines 55-60.	1-3, 5-7, 9-10
Y	US 4,075,069 A (SHINOHARA et al) 21 February 1978, col. 2, lines 18-60 and Figures.	1-3, 5-7, 9-10
A	US 4,522,695 A (NEEFE) 11 June 1985	1
A	US 5,112,465 A (DANIELSON) 12 May 1992	1



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

01 AUGUST 2000

Date of mailing of the international search report

06 SEP 2000

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

DONALD R. VALENTINE

Telephone No. (703) 308-0661

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**